



Influence of addition order and contact time on thorium(IV) retention by hematite in the presence of humic acids

Pascal E. Reiller, F. Casanova, V. Moulin

► To cite this version:

Pascal E. Reiller, F. Casanova, V. Moulin. Influence of addition order and contact time on thorium(IV) retention by hematite in the presence of humic acids. *Environmental Science and Technology*, 2005, 39 (6), pp.1641-1648. 10.1021/es048856h . cea-00288421

HAL Id: cea-00288421

<https://hal-cea.archives-ouvertes.fr/cea-00288421>

Submitted on 18 Aug 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives| 4.0 International License

Influence of addition order and contact time on thorium (IV) retention by hematite in the presence of humic acids.

Pascal Reiller, Florence Casanova*

CEA, CE Saclay, Nuclear Energy Division, DPC/SECR, Laboratoire de Spéciation des Radionucléides et des Molécules, bâtiment 391, BP 11, F-91191 Gif sur Yvette CEDEX, France.

Valérie Moulin

CEA, CE Saclay, Nuclear Energy Division, DDIN/MR, bâtiment 121, BP 11, F-91191 Gif sur Yvette CEDEX, France.

tel: +33-1-6908-4312, fax: +33 1 6908 5411

pascal.reiller@cea.fr

The influence of addition order and contact time in the system hematite ($\alpha\text{-Fe}_2\text{O}_3$) – humic acid (HA) – thorium (IV) was studied in batch experiments. Thorium (IV) is considered here as a chemical analogue of other actinides (IV). The sorption isotherms were acquired varying pH in the range 2-10, and HA concentration in the range 1-100 mg/L. As already observed by numerous authors, thorium (IV) retention was hindered when HA and hematite were equilibrated beforehand during 24 hours. As it has been observed in a previous study, this

effect was drastic when the ratio between humic and surface (iron oxide) sites exceeds a critical value. However, when HA were added after a 24 hours equilibration of the hematite-thorium (IV) system, thorium (IV) was barely desorbed from the iron oxide surface. Furthermore, no drastic effect of the ratio between humic and surface sites could be evidenced, as the increase of HA concentration only results in a slight monotonic decrease in Th(IV) retention. Increasing contact time between components of the systems only indicated slight Th(IV) retention variation. This was interpreted as a consequence of slow kinetic controls of both the Th(IV)-HA complexation and HA-hematite sorption.

Humic substances, humic acids, iron oxides, colloids, retention kinetics, thorium, tetravalent actinides, complexation.

Introduction

Organic colloids can enhance the mobilisation of metallic pollutants in soils and sediments (1-6). Sorption phenomena of natural organic matter (NOM) are of a great importance on this account. The general affinity of NOM and its humic fractions towards mineral surfaces not only induces modifications of physico-chemical properties, as surface potential or colloidal stability (7, 8), but also provokes modifications of the NOM itself (9-12).

Humic substances (HS) are the alkaline extractible fraction of NOM and are operationally defined from the extraction procedure: (i) humin is the insoluble fraction at whatever pH; (ii) humic acids (HA) are the insoluble fraction in acidic pH; (iii) fulvic acids (FA) are the soluble fraction whatever pH (sorbing on XAD resin) (13). HS can be now represented as aggregates of aromatic molecules (mostly phenolic) carrying a large number of carboxylic functions (14-16). The cohesion of these aggregates is through more or less weak bonding including van der Waals interactions or hydrogen bonding. Due their high functionality, HS can strongly complex multivalent elements and modify their retention by minerals (17-21).

The association of thorium (IV) with HA is strong and has been observed on the field (22-25), and quantified (26-28). Thorium (IV) is often used as a chemical analogue for the other actinides (IV) (29). Solubility of actinides (IV) is fairly constant within the series, *i.e.* 10^{-8} - 10^{-9} M if $\text{pH} \geq 4$ (30, 31). Thorium (IV) seems to be preferentially associated with the highest relative molecular weight fraction of the NOM, and this association seems to be kinetically governed (32, 33).

Humic acids are known to reduce redox sensitive actinides, *i.e.* Pa, Np and Pu (34-40), due either to the low redox potential of aqueous solution of HA (41-44) or/and by the preferential complexation of multicharged cations (45). The +IV oxidation state of the actinides seems to be stabilised by the humic complexation.

Thermodynamic description of the metallic cation retention by mineral surface in the presence of HA has often led to a deviation from additivity rules of interactions models (46-48), if the modelling is performed in a sufficiently wide parametric interval. Fractionation of HA induced by sorption on mineral surfaces should imply modification of HA aggregates and therefore modification of complexing properties of these aggregates. On the other hand, some authors have reported an influence of addition order. If the influence noted by Davis (19) was moderate in the case of Cu(II) on γ -alumina, it was clearly strong in the case of Zr-Hf(IV) on kaolinite (18). These authors compared the systems where (i) mineral surface and HA were pre-equilibrated before any addition of metallic cation, and (ii) mineral surface and metallic cation were equilibrated beforehand and HA was added afterwards. Liu and Gonzales (49) did not detect any noticeable difference when HA was pre-equilibrated or added simultaneously with divalent metals on montmorillonite, but the authors did not equilibrate the metal with the mineral surface beforehand.

For a predictive modelling of metal (IV) retention by mineral surface in the presence of HA, one has to understand the mechanism of these phenomena. Therefore, in order to illustrate the different cases we have studied the following pre-equilibrated systems: (i) hematite and HA equilibrated before any addition of Th(IV); (ii) hematite and Th(IV) equilibrated before any addition of HA, (iii) Th(IV) and HA pre-equilibrated before any addition of hematite

Experimental

Materials. The colloidal hematite suspension and humic acids were the same as the one used in previous studies (17, 50, 51). Briefly, hematite was obtained from AEA Harwell and characterised by Cromières *et al.* (50, 51) – diameter $D = 55$ nm, specific surface $S_{sp} = 19$ m²/g, Proton Exchange Capacity = 3.8×10^{-5} eq/g –; purified Aldrich HA was characterised by Kim *et al.* (52) – PEC = 5.4×10^{-3} eq/g –.

The initial solution of thorium (^{228}Th in 2 N HNO_3) was obtained from Amersham. This solution was diluted in order to obtain a 1.09×10^{-9} M stock solution in 0.9 M NaClO_4 and 0.2 M HNO_3 . All other chemicals were reagent grade, and Millipore filtered water purged with Ar(g) was used (Milli-Q).

pH measurement. The pH measurement was done using a TACUSSEL[®] pH-meter (PHM 220 MeterLab) with a combined TACUSSEL[®] electrode (Radiometer type XC 161, modified NaClO_4 0.1 M, NaCl 10^{-2} M). Calibration in $[\text{H}^+]$ is performed with commercial buffers (Prolabo, pH = 4, 7 and 9). The pH of the stock solution of colloidal hematite is about 1 which minimise the $\text{CO}_{2(\text{g})}$ dissolution. Nevertheless, the surface of solution was swept with Ar(g) , in order to minimise the dissolution of $\text{CO}_{2(\text{g})}$ in the suspensions.

Preparation of the suspension. The sorption experiments were conducted at room temperature according to a batch procedure in 10 ml polycarbonate vials sealed with screwcaps (Nalgene[®]).

Different *modus operandi* were used depending on the order of addition of the constituents. In all the experiments, the hematite suspension was always prepared first.

Hematite suspension. As the colloidal hematite suspension was stored under acidic conditions ($\text{pH} \cong 1$), the colloidal phase was rinsed with Milli-Q water in order to eliminate excess acid, and to eliminate the last traces of chloride ions. An aliquot of the initial solution (1.5 g.L^{-1}) was dispersed into Milli-Q water (9.5 ml) in centrifuge tubes and ultrasonically (Bioblock 35 kHz) shaken for 30 minutes. The obtained suspension was then ultracentrifuged at 50,000 rpm for 30 minutes and 6 ml of the supernatant were discarded: this operation is repeated 3 times. The concentration of the hematite suspension was fixed at the desired concentration by diluting the rinsed solution by the background electrolyte (NaClO_4). The pH was adjusted at the desired value. The obtained suspension was shaken for 24 hours to allow equilibration of the suspension.

Under the same conditions, inorganic carbon concentration has been estimated to be less than 5×10^{-5} M (53, 54), which induces only a weak influence on Th(IV) speciation (28, 55).

Depending on the order of addition, either HA or Th(IV) was added to the suspension.

HA addition. When the hematite suspension was equilibrated, aliquots of the HA stock solution were added. The pH value was adjusted using freshly prepared 0.1 M HClO₄ or NaOH, and shaken for the appropriate time.

Thorium (IV) addition. When the suspension was equilibrated, an aliquot of the thorium (IV) stock solution was added to obtain a final concentration of 1.15×10^{-12} M; the pH was adjusted at the desired value. The solution was shaken again for the appropriate time.

Separation of the colloidal suspension. As in previous studies (17, 28), we used the separation methods used by Cromières *et al.* (50), in order to minimise the thorium (IV) adsorption onto the vessel walls (54, 56). The retention was calculated referring to the activity measured in the suspension and not referring to the total activity introduced in the ultracentrifuge tube.

After the appropriate equilibrium time, three 0.5 mL aliquots of the suspension were sampled for thorium activity measurement (A_1 is the mean of the measurements). The colloids were separated from the liquid phase by ultracentrifugation (90 min, 50,000 rpm), the pH of the supernatant was measured, and three other aliquots of 0.5 mL were sampled from the supernatant for thorium activity measurement (A_2). The activities of ^{228}Th were measured by liquid scintillation counting. The sample aliquots were added to 4 mL of liquid scintillator (Ultima Gold AB). The activity measurements were performed after one month in order to attain the secular equilibrium of ^{228}Th with its daughters.

Sorption parameters. The sorption percentage R was calculated from the activities of the suspension (A_1) and of the supernatant (A_2) according to the following equation:

$$R (\%) = \left(1 - \frac{A_2}{A_1} \right) \times 100 \quad (1).$$

For the sake of comparison with independent results, the results are presented *vs.* the ratio of available binding site $[\equiv\text{HA}] \div [\equiv\text{SOH}]$ defined as:

$$\frac{[\equiv\text{HA}]}{[\equiv\text{SOH}]} = \frac{C_{\text{HA}} (\text{g/L}) \times 5.4 \cdot 10^{-3} (\text{eq/g})}{C_{\alpha\text{-Fe}_2\text{O}_3} (\text{g/L}) \times 3.8 \cdot 10^{-5} (\text{eq/g})} \quad (2),$$

where $[\equiv\text{HA}]$ is the concentration of humic sites, and $[\equiv\text{SOH}]$ is the concentration of surface sites.

Results and discussion

Pre-equilibration of hematite and HA. In figure 1 are reported pH isotherms obtained in Reiller *et al.* (17) for the systems where hematite (50 mg/L) and HA (0 and 10 mg/L) are pre-equilibrated for 24 hours (diamond symbols), before any addition of thorium (IV) at 0.1 and 10^{-3} mol NaClO₄/L . New data obtained for $[\alpha\text{-Fe}_2\text{O}_3] = 500$ mg/L at 0.1 mol NaClO₄/L are also reported (grey circles). Plotting these results in $K_d (\text{mL/g}) = [\text{Th}]_{\text{sorbed}}/[\text{Th}]_{\text{free}}$ (data not shown) show no differences with the results obtained in (17). Hence the sorption of Th(IV) on hematite can be directly compared in the two systems.

The results of HA retention in the systems were reported earlier (17).

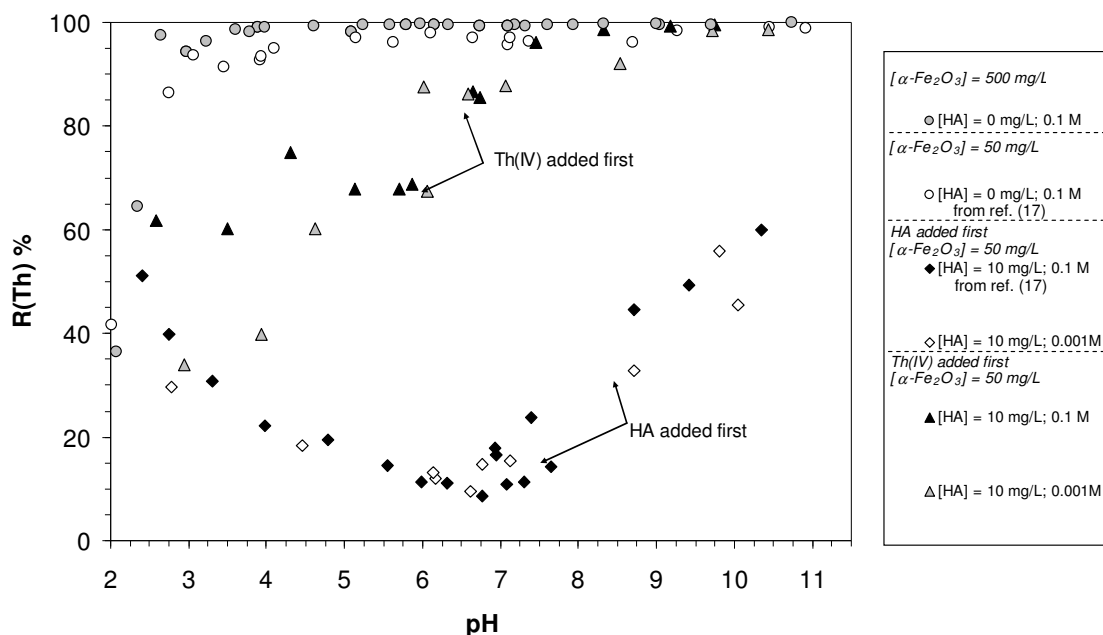


Figure 1: Influence of the addition order for the system hematite-HA-Th(IV) with 24 hours equilibration time: circles, no HA added; diamonds, HA added first; triangles, Th(IV) added first.

The decrease in metal retention when HA is pre-equilibrated with the solid is a classical observation (18-21, 57). Takahashi *et al.* (18) postulated that this phenomenon was due to the weak interaction of tetravalent cations, *i.e.* Zr(IV) and Hf(IV), with humic substances. The known interaction of thorium (IV) with natural organic matter observed in aquatic, marine and groundwater systems seems to contradict the latter hypothesis (22-24). Moreover, strong interaction constants were determined for Th(IV) and Np(IV) with humic acid in pH ranges relevant to natural waters (28, 58, 59). Thus, the strength of the interactions between HA and metal ions does not seem to be the main factor implied. Under our conditions, humic sites are mainly present in solution, and their concentration in solution increases with pH as ionisation increases. When Th(IV) is added in the system, competition occurs between free humic sites and hematite surface sites. This competition is strongly in favour of HA in acidic-neutral pH range – high strength of complexation between Th(IV) and HA –, whereas for $\text{pH} > 8$

complexation by surface sites increases up to 50%. Hence in this system, where hematite is pre-equilibrated with HA, organic matter controls Th(IV) behaviour.

Decreasing the ionic strength to 10^{-3} M (open diamonds on figure 1) does not seem to have any effect in this system. Similarly, ionic strength had no or very weak influence on HA retention onto this substrate as evidenced in the previous study (17). As a matter of fact, the actual colloidal state of this $\alpha\text{-Fe}_2\text{O}_3$ sample limits the effect of ionic strength (50, 60).

Up to now the tentative modelling of ternary systems, *i.e.* solid-humic-metal, revealed that the additivity rule cannot be simply applied (46-48). As a matter of fact, a large number of authors has clearly shown that slow sorption kinetic, fractionation phenomena and solid phase dissolution were implied (9, 12, 61-66). Thus, a reliable thermodynamic modelling of these systems is difficult to assess without prior assessment of an actual equilibrium state.

Pre-equilibration of hematite and Th(IV). The results obtained when Th(IV) is pre-equilibrated with hematite before any addition of HA (triangle symbols on figure 1) are illustrations of the modelling difficulty. The decrease in Th(IV) retention is clearly weaker than in the former case. This weaker influence of HA when added after hematite-metal equilibration was reported by only few authors (18, 19). The effect was not that spectacular in the case of Cu(II) on γ -alumina (19), but seems equivalent in the case of Zr(IV)/Hf(IV) on kaolinite (18). This effect was not detected in the case of silica by Takahashi *et al.* (18).

The influence of HA concentration on Th(IV) retention by colloidal hematite at different pH values reported by Reiller *et al.* (17) is reported on figure 2 using closed symbols. The equilibration time was 24 hours for hematite-HA suspension and 24 hours after the addition of Th(IV). Comparable batch experiments were performed but equilibrating Th(IV) with hematite for 24 hours prior to addition of HA in the suspension. The final suspension was then shaken for another 24 hours. The results are plotted using open symbol on figure 2.

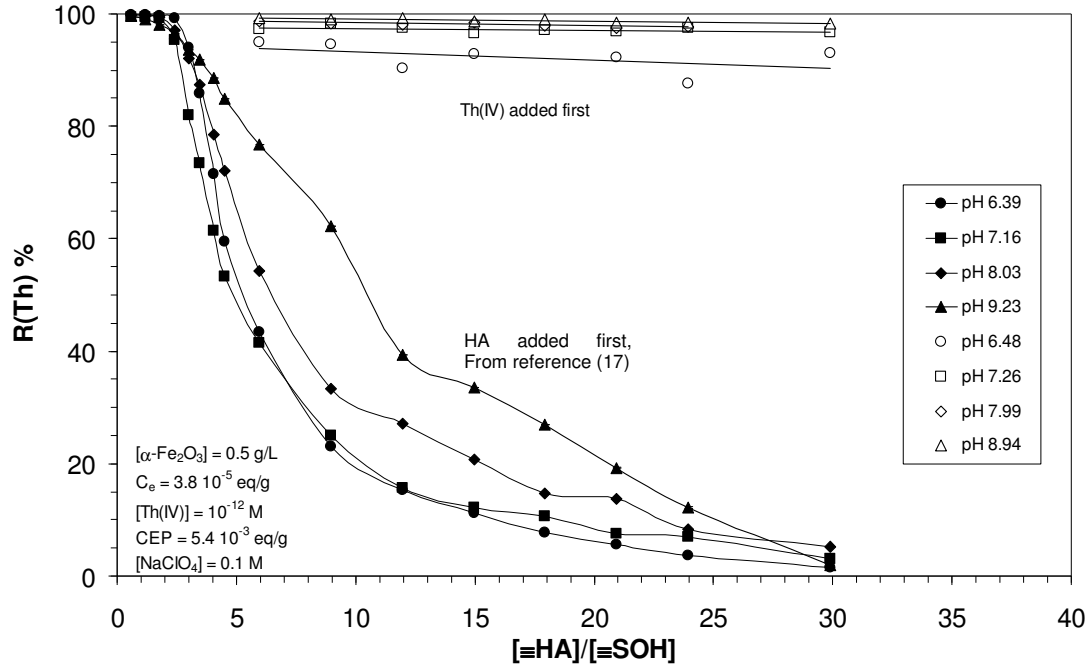


Figure 2: Influence of HA on the sorption of thorium (IV) onto hematite and of the addition order after 24 hours equilibration time. Closed symbols from (17): HA added first; open symbols: Th(IV) added first; $[\text{Th}] = 1 \times 10^{-12} \text{ M}$; $[\alpha\text{-Fe}_2\text{O}_3] = 500 \text{ mg.L}^{-1}$; $I = 0.1 \text{ M}$ (NaClO_4).

It was noted in Reiller *et al.* (17) that the organic layer at the hematite surface has a marked influence on the Th(IV) sorption when the ratio $[\equiv\text{HA}]/[\equiv\text{SOH}]$ was about 3. Such an effect could not be evidenced when Th(IV) is equilibrated with hematite before any HA addition. Even when $[\equiv\text{HA}]/[\equiv\text{SOH}] \approx 30$, $R(\text{Th})$ is only decreased from 99.6 % to 93 % at $\text{pH} \approx 6.5$. Thorium (IV) retention in these systems still seems to increase with pH in this interval, as it was in Reiller *et al.* (17), even if the $R(\text{Th})$ values could not be discriminated statistically. In to the study of Takahashi *et al.* (18) for the HA-kaolinite system, the ratio $[\equiv\text{HA}]/[\equiv\text{SOH}]$ can be calculated as:

$$\frac{[\equiv\text{HA}]}{[\equiv\text{SOH}]} = \frac{30 \cdot 10^{-3} \text{ (g/L)} \times 6.1 \cdot 10^{-3} \text{ (meq/g)}}{2 \text{ (g/L)} \times 2.9 \cdot 10^{-5} \text{ (eq/g)}} = 3.2.$$

This value is lower than the one used in this study ($[\equiv\text{HA}]/[\equiv\text{SOH}] \approx 30$). In the case of our hematite sample, no difference in the addition order could be anticipated at a ratio of 3.2 from the results in figure 2. Nevertheless, one should keep in mind that kaolinite is less efficient in retaining HA than hematite (18).

The results obtained are not easily interpreted. Nevertheless, given the preferential complexation of thorium (IV) by the highest molecular mass fraction of NOM (32, 33), and the kinetic control of the NOM sorption by mineral surface (12, 61, 66), a tentative explanation of this comportment can be proposed. Van de Weerd *et al.* (61) modelled the results of Gu *et al.* (12) and proposed different sorption kinetics for six fractions representing NOM: namely hydrophobic and hydrophilic fractions of size $< 3\text{kDa}$, $3\text{-}100\text{ kDa}$ and $> 100\text{ kDa}$. The lower mass fraction and the more hydrophobic fraction have faster kinetics. Through this modelling, the higher mass fractions reach sorption equilibrium in times ranging from 100 hours to more than 900 hours. These modelling results were experimentally confirmed by Hur and Schlautman (66) in the case of purified Aldrich humic acid

Interestingly, the hematite sample used by Gu *et al.* (12) and the one used in Reiller *et al.* (17) and in this study too, have very similar properties except for the size of the particles, *i.e.* $D = 150\text{-}300\text{ nm}$, $S_{\text{sp}} = 10\text{ m}^2/\text{g}$, Anion Exchange Capacity = $3.86 \times 10^{-5}\text{ mol/g}$. Nevertheless, the experiments of Gu *et al.* (12) were performed at $\text{pH} = 4.1$. The comparison of our results with Gu *et al.* (12) experiments and with van de Weerd *et al.* (61) modelling results, can only be qualitative. The experiments by Hur and Schlautman (66) could be compared to our results apart from the lack of site density determination and the difference in specific surface area ($7.41\text{ m}^2/\text{g}$).

In our case, no fraction $> 100\text{ kDa}$ can be anticipated with HA. But depending on the concentration, the fraction $3\text{-}100\text{ kDa}$ could reach sorption equilibrium after 500 hours for hydrophobic fractions and more than 900 hours for hydrophilic fractions (61). Given the short

time of our experiments (24 hours) the sorption of these fractions could have not reached equilibrium. This is further confirmed by the observation of Hur and Schlautman (66). Therefore, when HA are pre-equilibrated with hematite over 24 hours, the higher mass fractions are not in equilibrium with the hematite surface and are thus present in “solution”. When Th(IV) is added to this suspension the complexation with higher mass fractions would lead to its presence in the supernatant. Moreover, the formation of inner-sphere surface complexes of thorium (IV) on this hematite sample, evidenced by Cromières *et al.* (50), could help to explain this unexpected behaviour.

When Th(IV) is pre-equilibrated with hematite, the complexation between the higher mass fraction in solution and sorbed Th(IV) seems less probable in the time frame of the experiment, and the metal retention by hematite would be more important.

Gu *et al.* (12) used a 1% hematite stock solution, diluted to 1/5 (*i.e.* $\approx 2\text{g/L}$, or $[\equiv\text{SOH}] = 7.7 \times 10^{-5} \text{ eq/L}$), and the high concentration postulated by van de Weerd *et al.* (61) was 14.4 mg of carbon/L (12 meq/g of carbon, or $[\equiv\text{HA}] = 1.7 \times 10^{-4} \text{ eq/L}$). This leads to a ratio $[\equiv\text{HA}]/[\equiv\text{SOH}] = 2.24$. This value is very close to the retention drop evidenced in Reiller *et al.* (17). The experiments reported in figure 2 – $[\equiv\text{HA}]/[\equiv\text{SOH}] \geq 5$ – were thus performed in conditions where higher mass and hydrophobic fractions would not be in equilibrium with the hematite surface.

The question of Th(IV) sorption reversibility on the hematite sample must also be addressed also. Ho and Doern (67) showed that uranium (VI) was partly irreversibly bound onto hematite at $\text{pH} = 6.2$, where highly hydrolysed $(\text{UO}_2)_3(\text{OH})_5^+$ was the major specie under these conditions (31, 68). The total reversibility could only be obtained lowering pH to 4 within 24 h, where UO_2^{2+} is the major specie. Under our conditions, we can estimate, referring to Neck and Kim (30), that $\text{Th}(\text{OH})_3^+$ and $\text{Th}(\text{OH})_4(\text{aq})$ are the major thorium (IV) species in solution in the interval $6 \leq \text{pH} \leq 9$. As in the case of U(VI), the presence of strongly hydrolysed

Th(IV) species can be responsible of the irreversible process. However, studies on sorption reversibility of thorium (IV) are scarce and this phenomenon is difficult to take into account without a proper analysis.

Influence of contact time. The influence of slow kinetics in HA chemistry has been evidenced either in the case of metal complexation (33, 69), retention by mineral surface (12, 66), or even in the case of structural rearrangement (70, 71). Hence, contact time between HA and pre-equilibrated hematite-Th(IV) systems at $\text{pH} \approx 7$ was increased from 24 hours to 1, 2 and 3 weeks (168, 336 and 504 hours). Results are reported in figure 3 compared to the results of Reiller *et al.* (17) ($\alpha\text{-Fe}_2\text{O}_3\text{-HA}$ 24h - Th(IV) 24h; $\text{pH} = 7.16$, closed squares) and to the results presented in figure 2 ($\alpha\text{-Fe}_2\text{O}_3\text{-Th(IV)}$ 24 h – HA 24 h; $\text{pH} = 7.26$, open squares) obtained at about the same pH value. A slight decrease in the $R(\text{Th})$ value could be evidenced in figure 3 when contact time is increased. The differences between the different contact times are only statistically significant when $[\equiv\text{HA}]/[\equiv\text{SOH}] \geq 30$ ($R(\text{Th}) \pm 2.\sigma$). As in the previous cases, the sorption decrease is more intense when the ratio $[\equiv\text{HA}]/[\equiv\text{SOH}]$ increases. Nevertheless, the retention drop is undoubtedly less significant comparing to the Th(IV) sorption hindrance provoked by the formation of the organic layer as noted earlier (c.f. figure 2). These results indicate that the slow sorption, or complexation, kinetics has only minor effect in the time frame of these experiments. It can be suggested that a longer equilibration time could induce a more intense desorption of Th(IV) from hematite surface.

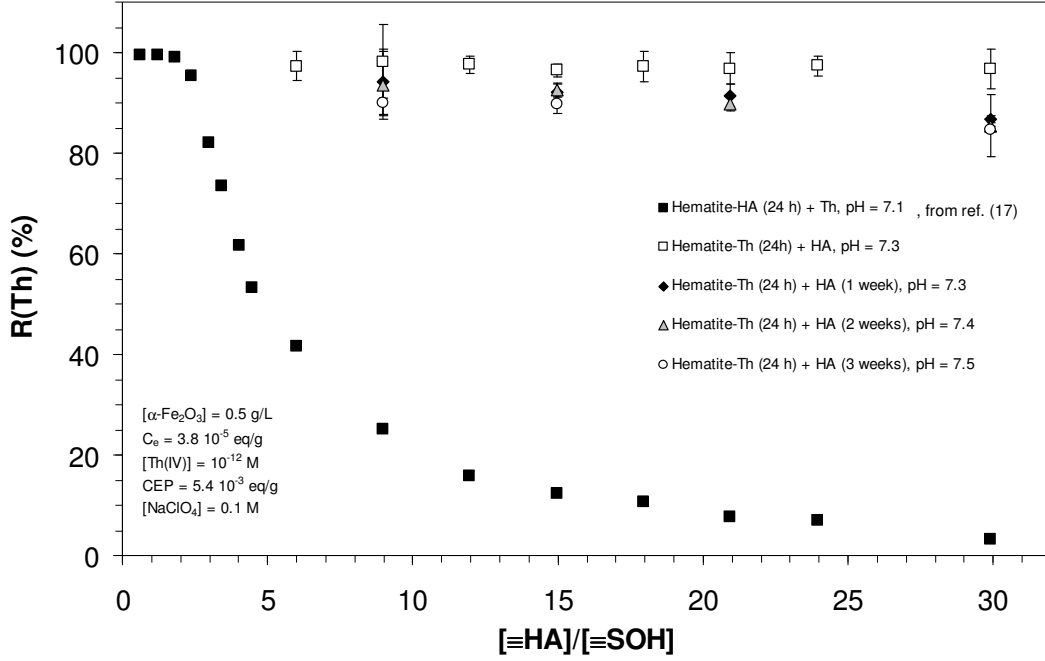


Figure 3: Influence of the addition order of the components, of the contact time and HA concentration on the retention of Th(IV) at pH \approx 7.

Quigley *et al.* (72) and Guo *et al.* (73) showed that the complexation of thorium (IV) is more intense for the hydrophilic fraction of marine organic matter, especially in the case of acid polysaccharides (size $\leq 0.5 \mu\text{m}$). In the model developed by van de Weerd *et al.* (61), the hydrophilic fractions have the slowest sorption kinetics. If thorium (IV) is preferentially complexed by higher sized and hydrophilic fractions, then the exchange between hematite surface and organics in solution seems not to be favoured, and thorium (IV) should be preferentially fixed on the solid in the time frame of the experiment.

Interestingly, studying the leaching of borosilicate glasses, Dran *et al.* (74) showed that, Zr(IV) was highly retained in the altered layer, but also leached from borosilicate glasses by solutions containing Aldrich humic acids as the concentration of Zr(IV) increased from $2.2 \times 10^{-7} \text{ M}$ – 0.02 mg Zr/L – with no HA, up to 1.1×10^{-6} – 0.1 mg Zr/L – with 80 mg HA/L. The authors also showed that the kinetic must be very slow at 90°C during 168 hours.

Pre-equilibration of HA and Th(IV) and influence of contact time. For these experiments, hematite concentration was lowered to 50 mg/L. The $[\equiv\text{HA}]/[\equiv\text{SOH}]$ ratio was the same as in figure 2 and figure 3, so the HA concentrations were lowered to the tenth of those used in Reiller *et al.* (17) (figure 4, closed squares). A similar retention pattern is obtained (figure 4, grey squares). Nevertheless, it can be observed that the retention of Th(IV) is slightly higher in this series than in the one previously obtained. These differences cannot be interpreted, and further work is in progress to understand this behaviour.

The modelling of the interaction between metallic cations and HA has recently been presented as kinetically controlled (69). This kinetic control seems to lead to an irreversible part of the complexation. This seems to be in agreement with the complexation of Th(IV) in marine systems (33).

The influence of contact time between HA and thorium (IV) on the retention by $\alpha\text{-Fe}_2\text{O}_3$ at $\text{pH} \approx 7$, as well as the results obtained in Reiller *et al.* (17) for the same conditions, are reported on figure 4a. As in the preceding cases, the contact time in the time frame of the experiments has only a weak influence on the final result. Nevertheless, a slight increase of Th(IV) retention by the solid phase can be noticed. This effect is barely statically significant.

In these experiments, the contact times between HA and hematite are the same, *i.e.* 24 hours. Consequently, these results only reflect the Th(IV) complexation by HA, assuming no effect on HA properties. Von Wandruszka *et al.* (71) evidenced an enhancement of the pyrene fluorescence in Th(IV)-HA systems when $[\text{Th(IV)}] > 10^{-5} \text{ M}$, indicating further aggregation of HA samples, but, as no pH indication is available in the original paper, the influence of ThO_2 solubility cannot be checked. Nevertheless, no such effect could be anticipated under our conditions where $[\text{Th(IV)}] \approx 10^{-12} \text{ M}$.

The influence of contact time between Th(IV)-HA complex and hematite surface is reported on figure 4b. In these series of experiments, Th(IV)-HA complex is equilibrated during about

1 month (29 and 34 days) before any contact with hematite. The contact time of the pre-equilibrated Th(IV)-HA complex with hematite was increasing to 9 and 28 days (open symbols). The results obtained in Reiller *et al.* (17) (black squares), and the ones that were reported on figure 4a (hematite-HA 24 h / Th(IV) 24 h, grey squares; Th(IV)-HA 37 days / hematite 24 h, grey circles) are reported for the sake of comparison.

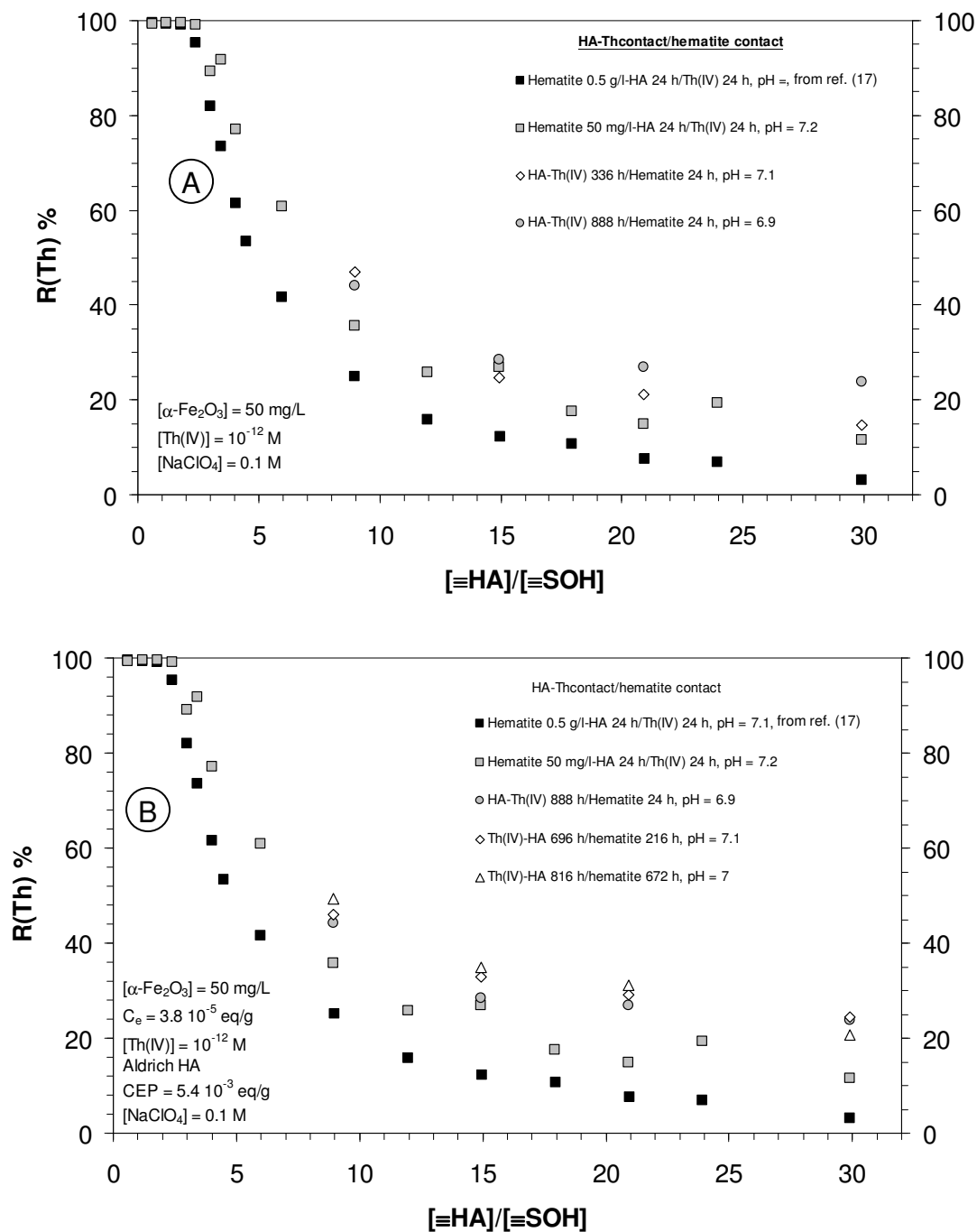


Figure 4: Influence of contact time and HA concentration at $\text{pH} \approx 7$, in the systems: a. hematite-HA pre-equilibrated followed by Th(IV) addition; b. Th(IV)-HA pre-equilibrated for 1 month followed by hematite addition.

As in figure 4a, a slight increase in Th(IV) retention can be observed when increasing contact time of the humic complex with hematite. Nevertheless, as in figure 4a, this increase

is barely statistically significant. A tentative explanation could be linked to the discussion of preferential complexation of Th(IV) by higher mass fraction and to the kinetics control of Th(IV)-HA complex. On the one hand, it has been proposed that thorium (IV) is preferentially complexed by the higher sized and hydrophilic fractions of NOM (72). On the other hand, from the works of van de Weerd *et al.* (61), these fractions have the slowest sorption kinetic that would imply not only a slow desorption of thorium (IV) from hematite surface, but also a slow sorption of pre-equilibrated Th(IV)-HA complex on the same hematite surface. A final step would be increasing contact times to larger values in order to test this hypothesis. Further works are in progress to test the validity of this hypothesis.

Acknowledgment

This work has been carried out in the framework of the “HUMICS project” (FI4W-CT96-0027) and “HUPA project” (FIKW-CT-2001-00128), and MRTRA project of the Risk Control Domain (CEA/DEN/DDIN).

References

- (1) Miekeley, N.; Vale, M. G. R.; Tavares, T. M.; Lei, W., Some aspects of the influence of surface and ground water chemistry on the mobility of thorium in the "Morro do Ferro" - environment. *Mat. Res. Soc. Symp. Proc.* **1982**, *11*, 725-733.
- (2) Fujikawa, Y.; Zheng, J.; Cayer, I.; Sugahara, M.; Takigami, H.; Kudo, A., Strong association of fallout plutonium with humic and fulvic acid as compared to uranium and ^{137}Cs in Nishiyama soils from Nagasaki, Japan. *J. Radioanal. Nucl. Chem.* **1999**, *240*, 69-74.
- (3) Kersting, A. B.; Efur, D. W.; Finnegan, D. L.; Rokop, D. J.; Smith, D. K.; Thompson, J. L., Migration of plutonium in groundwater at the Nevada Test Site. *Nature* **1999**, *397*, 56-58.

- (4) Santschi, P. H.; Roberts, K. A.; Guo, L. D., Organic nature of colloidal actinides transported in surface water environments. *Environ. Sci. Technol.* **2002**, *36*, 3711-3719.
- (5) Wood, S. A., The role of humic substances in the transport and fixation of metals of economic interest (Au, Pt, Pd, U, V). *Ore Geol. Rev.* **1996**, *11*, 1-31.
- (6) Artinger, R.; Kienzler, B.; Schu ler, W.; Kim, J. I., Effects of humic substances on the ²⁴¹Am migration in a sandy aquifer: column experiments with Gorleben groundwater/sediment systems. *J. Contam. Hydrol.* **1998**, *35*, 261-275.
- (7) Kretzschmar, R.; Sticher, H., Transport of humic-coated iron oxide colloids in a sandy soil: Influence of Ca²⁺ and trace metals. *Environ. Sci. Technol.* **1997**, *31*, 3497-3504.
- (8) Kretzschmar, R.; Hesterberg, D.; Sticher, H., Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. *Soil Sci. Soc. Am. J.* **1997**, *61*, 101-108.
- (9) Meier, M.; Namjesnik-Dejanovic, K.; Maurice, P.; Chin, Y.-P.; Aiken, G. R., Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chem. Geol.* **1999**, *157*, 275-284.
- (10) Zhou, Q.; Maurice, P. A.; Cabaniss, S., Size fractionation upon adsorption of fulvic acid on goethite: equilibrium and kinetic study. *Geochim. Cosmochim. Acta* **2001**, *65*, 803-812.
- (11) Korshin, G. V.; Benjamin, M. M.; Sletten, R. S., Adsorption of natural organic matter (NOM) on iron oxide: Effects on NOM composition and formation of organo-halide compounds during chlorination. *Water Res.* **1997**, *31*, 1643-1650.

- (12) Gu, B.; Schmitt, J.; Chem, Z.; Liang, L.; McCarthy, J. F., Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* **1994**, 28, 38-46.
- (13) MacCarthy, P., The principles of humic substances. *Soil Science* **2001**, 166, 738-751.
- (14) Plancque, G.; Amekraz, B.; Moulin, V.; Toulhoat, P.; Moulin, C., Molecular structure of fulvic acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* **2001**, 15, 827-835.
- (15) McIntyre, C.; McRae, C.; Jardine, D.; Batts, B. D., Identification of compound classes in soil and peat fulvic acids as observed by electrospray ionization tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2002**, 16, 1604-1609.
- (16) Moulin, V.; Reiller, P.; Amekraz, B.; Moulin, C., Direct characterization of iodine covalently bound to fulvic acids by electrospray mass spectrometry. *Rapid Commun. Mass Spectrom.* **2001**, 15, 2488-2496.
- (17) Reiller, P.; Moulin, V.; Casanova, F.; Dautel, C., Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Appl. Geochem.* **2002**, 17, 1551-1562.
- (18) Takahashi, Y.; Minai, Y.; Ambe, S.; Makide, Y.; Ambe, F., Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique - A comparison with dissolved aluminum. *Geochim. Cosmochim. Acta* **1999**, 63, 815-836.
- (19) Davis, J. A., Complexation of trace metals by adsorbed natural organic matter. *Geochim. Cosmochim. Acta* **1984**, 48, 679-691.

- (20) Zachara, J. M.; Resch, C. T.; Smith, S. C., Influence of humic substances on Co^{2+} sorption by a subsurface mineral separate and its mineralogic components. *Geochim. Cosmochim. Acta* **1994**, 58, 553-566.
- (21) Labonne-Wall, N.; Moulin, V.; Villarem, J.-P., Retention properties of humic substances onto amorphous silica: consequences for the sorption of cations. *Radiochim. Acta* **1997**, 79, 37-49.
- (22) Miekeley, N.; Dotto, R. M.; Kuchler, I. L.; Insalta, P., The importance of organic compounds on the mobilization and bioassimilation of thorium in the Morro do Ferro environment. *Mat. Res. Soc. Symp. Proc.* **1985**, 44, 591-597.
- (23) Zeh, P.; Kim, J. I.; Buckau, G. In *OECD NEA Proceedings*, 1995; pp 81.
- (24) Dai, M. H.; Benitez-Nelson, C. R., Colloidal organic carbon and ^{234}Th in the Gulf of Maine. *Mar. Chem.* **2001**, 74, 181-196.
- (25) Guo, L. D.; Santschi, P. H.; Baskaran, M., Interactions of thorium isotopes with colloidal organic matter in oceanic environments. *Colloid Surf. A-Physicochem. Eng. Asp.* **1997**, 120, 255-271.
- (26) Nash, K. L.; Choppin, G. R., Interaction of humic and fulvic acids with Th(IV). *J. Inorg. Nucl. Chem.* **1980**, 42, 1045-1050.
- (27) Choppin, G. R.; Allard, B. Complexes of actinides with naturally occurring organic compounds. In *Handbook on the Physics and Chemistry of the Actinides*; Freeman, A. J., Keller, C., Eds.; Elsevier, 1985; pp 407-429.

- (28) Reiller, P.; Moulin, V.; Casanova, F.; Dautel, C., On the study of Th(IV)-humic acid interactions by competition sorption studies with silica and determination of global interaction constants. *Radiochim. Acta* **2003**, *91*, 513-524.
- (29) Choppin, G. R., Utility of oxidation state analogs in the study of plutonium behavior. *Radiochim. Acta* **1999**, *85*, 89-96.
- (30) Neck, V.; Kim, J. I., Solubility and hydrolysis of tetravalent actinides. *Radiochim. Acta* **2001**, *89*, 1-16.
- (31) Guillaumont, R.; Fanghänel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D. A.; Rand, M. *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*; North-Holland: Amsterdam, 2003; Vol. 5.
- (32) Zhang, Y. J.; Bryan, N. D.; Livens, F. R.; Jones, M. N., Selectivity in the complexation of actinides by humic substances. *Env. Poll.* **1997**, *96*, 361-367.
- (33) Quigley, M. S.; Santschi, P. H.; Guo, L. D.; Honeyman, B. D., Sorption irreversibility and coagulation behavior of ^{234}Th with marine organic matter. *Mar. Chem.* **2001**, *76*, 27-45.
- (34) Nash, K. L.; Fried, S.; Friedman, A. M.; Sullivan, J. C., Redox behavior, complexing, and adsorption of hexavalent actinides by humic acid and selected clays. Storing marine disposal of high-level radioactive waste. *Environ. Sci. Technol.* **1981**, *15*, 834-837.
- (35) Kim, J. I.; Delakowitz, B.; Zeh, P. D.; Koltz, D.; Lazik, D., A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. *Radiochim. Acta* **1994**, *66/67*, 165-171.
- (36) Marquardt, C.; Herrman, G.; Trautmann, N., Complexation of neptunium(V) with humic acids at very low concentrations. *Radiochim. Acta* **1996**, *73*, 119-126.

- (37) Pirlet, V.; van Iseghem, P.; Dierckx, A.; Desreux, J.-F., The investigation of the neptunium complexes formed upon interaction of high level waste glass and Boom Clay media. *J. Alloys Comp.* **1998**, 271, 267-271.
- (38) Zeh, P.; Kim, J. I.; Marquardt, C. M.; Artinger, R., The reduction of Np(V) in groundwater rich in humic substances. *Radiochim. Acta* **1999**, 87, 23-28.
- (39) André, C.; Choppin, G. R., Reduction of Pu(V) by humic acid. *Radiochim. Acta* **2000**, 88, 613-616.
- (40) Kuczewski, B.; Marquardt, C. M.; Seibert, A.; Geckeis, H.; Kratz, J. V.; Trautmann, N., Separation of plutonium and neptunium species by capillary electrophoresis-inductively coupled plasma-mass spectrometry and application to natural groundwater samples. *Anal. Chem.* **2003**, 75, 6769-6774.
- (41) Zauzig, J.; Stepniewski, W.; Horn, R., Oxygen concentration and redox potential gradient in unsaturated model soil aggregates. *Soil Sci. Soc. Am. J.* **1993**, 57, 908-916.
- (42) Österberg, R.; Shirshova, L., Oscillating, nonequilibrium redox properties of humic acids. *Geochim. Cosmochim. Acta* **1997**, 61, 4599-4604.
- (43) Matthiessen, A. Evaluating the redox capacity and the redox potential of humic acids by redox titrations. In *Humic substances in the global environment and implications on human health*; Senesi, N., Miano, T. M., Eds.; Elsevier, 1994; pp 187-192.
- (44) Struyk, Z.; Sposito, G., Redox properties of standard humic acids. *Geoderma* **2001**, 102, 329-346.
- (45) Kerndorff, H.; Schnitzer, M., Sorption of metals on humic acid. *Geochim. Cosmochim. Acta* **1980**, 44, 1701-1708.

- (46) Vermeer, A. W. P.; McCulloch, J. K.; van Riemsdijk, W. H.; Koopal, L. K., Metal ion adsorption to complexes of humic acid and metal oxides: deviation from the additivity rule. *Environ. Sci. Technol.* **1999**, *33*, 3892-3897.
- (47) Robertson, A. P., Goethite/humic acid interactions and their effects on copper(II) binding. Stanford University, 1996.
- (48) Christl, I.; Kretzschmar, R., Interaction of copper and fulvic acid at the hematite-water interface. *Geochim. Cosmochim. Acta* **2001**, *65*, 3435-3442.
- (49) Liu, A.; Gonzalez, R. D., Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *J. Colloid Interface Sci.* **1999**, *218*, 225-232.
- (50) Cromières, L.; Moulin, V.; Fourest, B.; Guillaumont, R.; Giffaut, E., Sorption of thorium onto hematite colloids. *Radiochim. Acta* **1998**, *82*, 249-256.
- (51) Cromières, L.; Moulin, V.; Fourest, B.; Giffaut, E., Physico-chemical characterization of the colloidal hematite/water interface: experimentation and modelling. *Colloid Surf. A-Physicochem. Eng. Asp.* **2002**, *202*, 101-115.
- (52) Kim, J. I.; Buckau, G.; Klenze, R.; Rhee, D. S.; Wimmer, H. "Characterisation and complexation of humic acids," EUR 13181, Commission of the European Communities, Brussels, 1991.
- (53) Labonne, N., Rôle des matières organiques dans les phénomènes de rétention des actinides sur la silice N° 4601 13 décembre 1993. Paris XI Orsay, 1993.
- (54) Cromières, L., Sorption d'éléments lourds (U(VI), Np(V), Th(IV), Am(III), Co(II), Cs(I), I(-I)) sur des colloïdes d'hématite. Paris XI-Orsay, 1996.

- (55) Östhols, E.; Bruno, J.; Grenthe, I., On the influence on mineral dissolution: III. The solubility of microcrystalline ThO₂ in CO₂-H₂O media. *Geochim. Cosmochim. Acta* **1994**, *58*, 613-623.
- (56) Rydberg, J.; Rydberg, B., Adsorption on glass and polythene from solution of thorium and thorium complexes in tracer concentration. *Sv. Kem. Tidskr.* **1952**, *64*, 200-211.
- (57) Ticknor, K. V.; Vilks, P.; Vandergraaf, T. T., The effect of fulvic acid on the sorption of actinides and fission products on granite and selected minerals. *Appl. Geochem.* **1996**, *11*, 555-565.
- (58) Pirlet, V.; Delécaut, G. In *9th International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03. September 21-26, 2003*; Gyeongju, Korea, 2003; pp 222.
- (59) Reiller, P., Prognosticating the humic complexation for redox sensitive actinides through analogy, using the charge neutralisation model. *Radiochim. Acta* **2004**, *in press*.
- (60) Hunter, K. A.; Hawke, D. J.; Choo, L. K., Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochim. Cosmochim. Acta* **1988**, *52*, 627-636.
- (61) van de Weerd, H.; van Riemsdijk, W. H.; Leijnse, A., Modelling the dynamic adsorption/desorption of NOM mixture: Effects of physical and chemical heterogeneity. *Environ. Sci. Technol.* **1999**, *33*, 1675-1681.
- (62) van de Weerd, H.; van Riemsdijk, W. H.; Leijnse, A., Modeling transport of a mixture of natural organic molecules: Effects of dynamic competitive sorption from particle to aquifer scale. *Water Resour. Res.* **2002**, *38*, 3301-3319.

- (63) Kaiser, K.; Zech, W., Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. *Soil Sci. Soc. Am. J.* **1997**, *61*, 64-69.
- (64) Rose, J.; Vilge, A.; Olivie-Lauquet, G.; Masion, A.; Fréchou, C.; Bottero, J. Y., Iron speciation in natural organic matter colloids. *Colloid Surf. A-Physicochem. Eng. Asp.* **1998**, *136*, 11-19.
- (65) Vilgé-Ritter, A.; Rose, J.; Masion, A.; Bottero, J. Y.; Laine, J. M., Chemistry and structure of aggregates formed with Fe-salts and natural organic matter. *Colloid Surf. A-Physicochem. Eng. Asp.* **1999**, *147*, 297-308.
- (66) Hur, J.; Schlautman, M. A., Molecular weight fractionation of humic substances by adsorption onto minerals. *J. Colloid Interface Sci.* **2003**, *264*, 313-321.
- (67) Ho, C. H.; Doern, D. C., The sorption of uranyl species on a hematite sol. *Can. J. Chem.* **1985**, *63*, 1100-1104.
- (68) Grenthe, I.; Fuger, L.; Konings, R. G. M.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical thermodynamics of uranium*; North-Holland: Amsterdam, 1992; Vol. 1.
- (69) Warwick, P. W.; Hall, A.; Pashley, V.; Bryan, N. D.; Griffin, D., Modelling the effect of humic substances on the transport of europium through porous media: a comparison of equilibrium and equilibrium/kinetic models. *J. Contam. Hydrol.* **2000**, *42*, 19-34.
- (70) Engebretson, R. R.; von Wandruszka, R., Kinetic aspects of cation-enhanced aggregation in aqueous humic acids. *Environ. Sci. Technol.* **1998**, *32*, 488-493.
- (71) von Wandruszka, R.; Ragle, C.; Engebretson, R., The role of selected cations in the formation of pseudomicelles in aqueous humic acid. *Talanta* **1997**, *44*, 805-809.

(72) Quigley, M. S.; Santschi, P. H.; Hung, C. C.; Guo, L. D.; Honeyman, B. D., Importance of acid polysaccharides for Th-234 complexation to marine organic matter. *Limnol. Oceanogr.* **2002**, *47*, 367-377.

(73) Guo, L. D.; Hung, C. C.; Santschi, P. H.; Walsh, I. D., Th-234 scavenging and its relationship to acid polysaccharide abundance in the Gulf of Mexico. *Mar. Chem.* **2002**, *78*, 103-119.

(74) Dran, J.-C.; Lombardi, J.; Magonthier, M. C.; Moulin, V.; Petit, J. C.; Trotignon, L., Leaching of borosilicate glasses by solutions containing humic acids: behaviour of metallic elements. *Radiochim. Acta* **1992**, *58/59*, 17-20.